



TITLE:

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CITATION:

Hashimoto, Tadanori ...[et al]. Third-Order Nonlinear Optical Properties of Sol-Gel Derived FeTiO Thin Films. Bulletin of the Institute for Chemical Research, Kyoto University 1994, 71(4-6): 420-429

ISSUE DATE:

1994-02-25

URL:

<http://hdl.handle.net/2433/77539>

RIGHT:

Third-Order Nonlinear Optical Properties of Sol-Gel Derived FeTiO₃ Thin Films

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Received November 12, 1993

Third-order nonlinear optical properties of sol-gel derived FeTiO₃ thin films have been investigated by the third-harmonic generation (THG) method, and the effect of valence of Fe ions on the third-order nonlinear optical susceptibility, $\chi^{(3)}$, has been examined. The $\chi^{(3)}$ value of FeTiO₃ thin film was 3.3×10^{-12} esu, which is comparable to those for TiO₂ polymorphs (rutile and anatase) but one order of magnitude lower than that of α -Fe₂O₃. Second-hyperpolarizability per Fe²⁺O formula unit, $\gamma(\text{Fe}^{2+}\text{O})$, was one fourth to one third of $\gamma(\text{Fe}_{2/3}^{3+}\text{O})$ and about four times as large as $\gamma(\text{Ti}_{1/2}^{4+}\text{O})$, indicating that the $\chi^{(3)}$ value of FeTiO₃ may be dominated by the $\gamma(\text{Fe}^{2+}\text{O})$ rather than $\gamma(\text{Ti}_{1/2}^{4+}\text{O})$.

KEY WORDS: FeTiO₃/ $\chi^{(3)}$ / Second-hyperpolarizability/ Sol-gel method

1. INTRODUCTION

As previously reported,¹⁾ the third-order nonlinear optical susceptibility, $\chi^{(3)}$, of the sol-gel derived α -Fe₂O₃ thin film was 5.8×10^{-11} esu, which is about 600 times as high as that of α -Al₂O₃ single crystal with the same corundum structure. This was ascribed to the much higher refractive index of α -Fe₂O₃ than that of α -Al₂O₃ on the basis of Miller's rule^{2,3)} which predicts that a material with high refractive index shows a high $\chi^{(3)}$. Since Fe element which is a transition metal having *d* electrons may be responsible for the high $\chi^{(3)}$,¹⁾ the effect of valence or *d* electronic structure of Fe ions on the third-order nonlinear optical properties is also of great interest. FeTiO₃ (ilmenite) was selected as a Fe²⁺-containing compound, in which both Fe²⁺ and Ti⁴⁺ ions are substituted for Al³⁺ ions in α -Al₂O₃. In addition, it should be noted here that α -Fe₂O₃¹⁾ and TiO₂⁴⁾ with high refractive index more than 2.5 are known to exhibit very high $\chi^{(3)}$ of 10^{-12} to 10^{-11} esu.

In the present study, FeTiO₃ thin films have been prepared on the SiO₂ glass substrates by the sol-gel method. Third-order nonlinear optical properties of the FeTiO₃ thin films have been investigated by the third-harmonic generation (THG) method and the effect of valence of Fe ions on the third-order nonlinear optical susceptibility has been examined.

2. EXPERIMENTAL

2.1 Preparation of FeTiO₃ thin films

FeTiO₃ thin films were prepared by the sol-gel method. As starting solution,

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$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} - \text{Ti}(\text{OC}_3\text{H}_7)_4 - \text{CH}_3\text{OCH}_2\text{CH}_2\text{OH} - \text{CH}_3\text{COCH}_2\text{COCH}_3$ solutions were selected. The chemical composition of the solution was 1 : 1 : 40 : 4 in molar ratio. Iron (III) nitrate enneahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was first dissolved in a solution of 2,4-pentanedione ($\text{CH}_3\text{COCH}_2\text{COCH}_3$) and half of a prescribed amount of 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$). Then, titanium isopropoxide ($\text{Ti}(\text{OC}_3\text{H}_7)_4$) which was diluted by the remainder of $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ in advance was mixed with the solution. Coating solutions were allowed to stand at 60°C for 24 h prior to use.

Dip-coating was used for film formation. A SiO_2 glass substrate was immersed in a coating solution, and pulled up at a rate of 3 cm min⁻¹. The film was heated at 800°C for 10 min immediately after each coating procedure. This cycle was repeated 10 times to attain the desired film thickness of about 0.3 μm. To enhance the laser-induced damage threshold (LIDT),⁵⁾ a SiO_2 coating was further applied onto the FeTiO_3 film. Otherwise, a part of FeTiO_3 film peeled off upon laser irradiation. In the present coating process, films are formed on both surfaces of the SiO_2 glass substrate. The FeTiO_3 and additional SiO_2 films on one surface were removed to minimize the interference effect⁶⁾ of THG light in the THG measurement.

2.2 Characterization of FeTiO₃ thin films

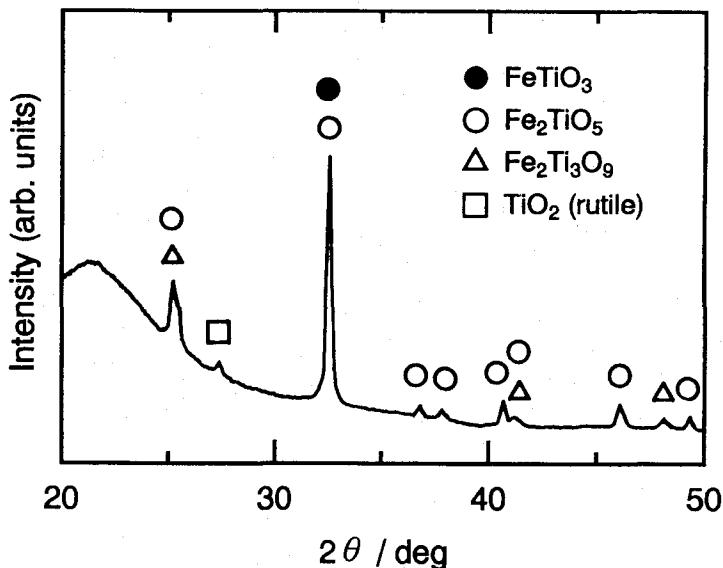
The crystalline phases precipitated in the FeTiO_3 thin film were identified by X-ray diffraction method using $\text{CuK}\alpha$ radiation. The refractive index of FeTiO_3 film was determined by an ellipsometer in the wavelength region from 500 to 1,000 nm. The ellipsometry measurement also gave the film thickness. The absorption spectra of FeTiO_3 films with and without additional SiO_2 coating were measured in the wavelength region from 200 to 2,000 nm by a UV-visible spectrophotometer.

THG measurement of FeTiO_3 thin film was made by means of a nonlinear optical measurement apparatus (Tokyo Instruments, Inc., Tokyo, Japan). The Q-switched Nd:YAG laser was operated at the fundamental wavelength of 1,064 nm with a pump pulse duration of 10 ns and a peak power density of 200 MW cm⁻². The laser frequency at 1,900 nm was obtained directly by stimulated Raman scattering in a high pressure hydrogen cell, which was excited by the Nd:YAG line at 1,064 nm. The THG light at 633 nm, which was isolated by a monochromator, was detected by a photomultiplier connected to a box-car integrator. The sample was mounted on a goniometer and rotated at 0.25° intervals from -40 to +40° by a computer-controlled stepper motor with respect to the axis perpendicular to the incident light.

In both absorption spectrum and THG measurements, the samples were irradiated from the side without films.

3. RESULTS

Figure 1 shows X-ray diffraction pattern of FeTiO_3 thin film. The main crystalline phase was FeTiO_3 (ilmenite) although small amounts of Fe_2TiO_5 (pseudobrookite), $\text{Fe}_2\text{Ti}_3\text{O}_9$ (pseudorutile) and TiO_2 (rutile) phases were precipitated. In the present study, Ti-containing solution was mixed with Fe-containing solution. The reversed mixing lead to the increased TiO_2 phase. The reducing treatment of the resultant film was attempted in order to convert the residual Fe^{3+} to Fe^{2+} ions. Although impurity phases such as Fe_2TiO_5 and $\text{Fe}_2\text{Ti}_3\text{O}_9$ decreased, the film became slightly blackish in color probably due to the formation of the reduced

Fig. 1. X-ray diffraction pattern of FeTiO₃ thin film.

species such as Fe metal or Ti³⁺ ion, which could not be detected by an X-ray diffraction. The crystallite size in the FeTiO₃ film was 30 nm.

3.1 Refractive index and optical transmittance

The wavelength dependence of refractive index, n , for FeTiO₃ thin film is shown in Figure 2. It is seen that the refractive index of FeTiO₃ film decreases with increasing wavelength. Figure 3 presents a linear plot of $(n^2 - 1)^{-1}$ versus E^2 for FeTiO₃ thin film based on Wemple's equation⁷⁾

$$\frac{1}{n^2 - 1} = \frac{E_0}{E_d} - \frac{E^2}{E_0 E_d}, \quad (1)$$

where E , E_0 and E_d are the photon energy, the average oscillator energy and dispersion energy in eV unit, respectively. E_0 and E_d are important optical properties of materials⁷⁾. The refractive indices of FeTiO₃ film were estimated as $n_{3\omega} = 2.33$ at 633 nm and $n_{\omega} = 2.17$ at 1,900 nm, and the coherence length, $l_c = 1.9/[6(n_{3\omega} - n_{\omega})]$, was 2.0 μm . The thickness of the FeTiO₃ film obtained by 10 dippings was typically 0.27 μm .

Figure 4 shows the absorption spectra of FeTiO₃ thin films with and without additional SiO₂ coating. Both spectra have a number of mountains and troughs arising from the interference of light. It is seen that the additional SiO₂ coating reduces the optical loss due to reflection especially in the wavelength region above about 400 nm. Fe²⁺ and Fe³⁺ ions in octahedral coordination are known to show absorption bands around 1,100 and 800 nm, respectively.⁸⁾ The difference in absorbance due to reflection loss between both spectra is relatively small around 1,100 and 800 nm, indicating that the present FeTiO₃ film includes Fe³⁺-containing compounds in accordance with the result of X-ray diffraction measurement. The optical band gap, E_g , of FeTiO₃ film was estimated to be 2.2 eV.

3.2 Evaluation of $\chi^{(3)}$ value

The THG intensities as a function of the rotation angle are given for (a) FeTiO₃ film and (b)

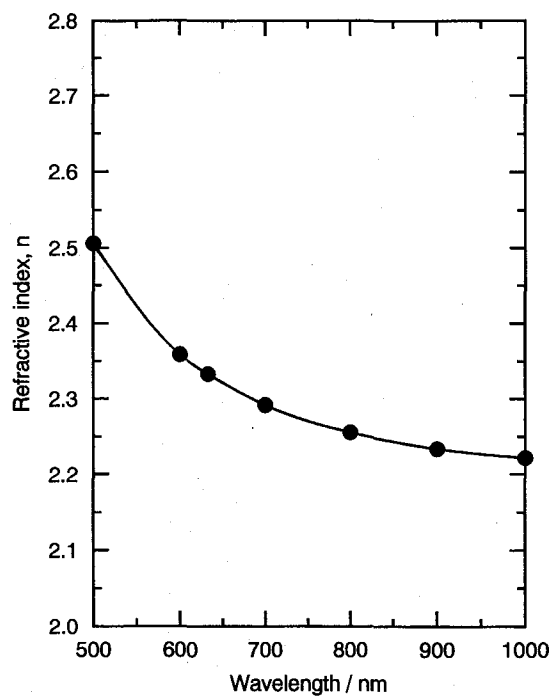


Fig. 2. Wavelength dependence of refractive index, n , for FeTiO_3 thin film.

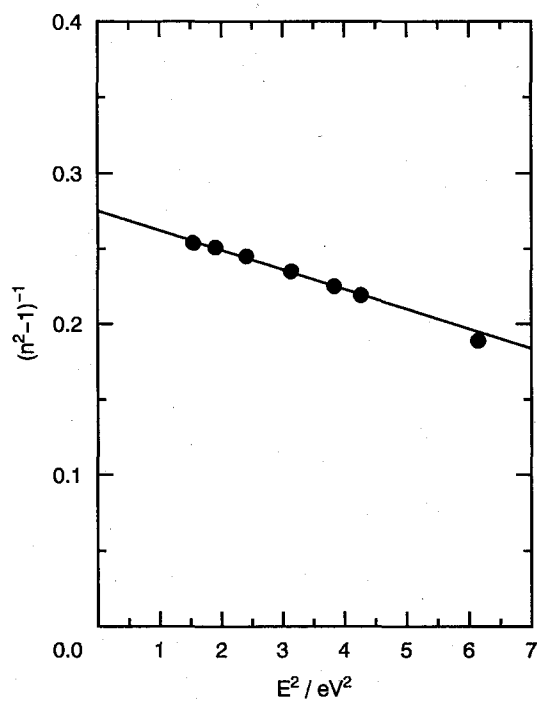


Fig. 3. A Linear plot of $(n^2-1)^{-1}$ versus E^2 for FeTiO_3 thin film.

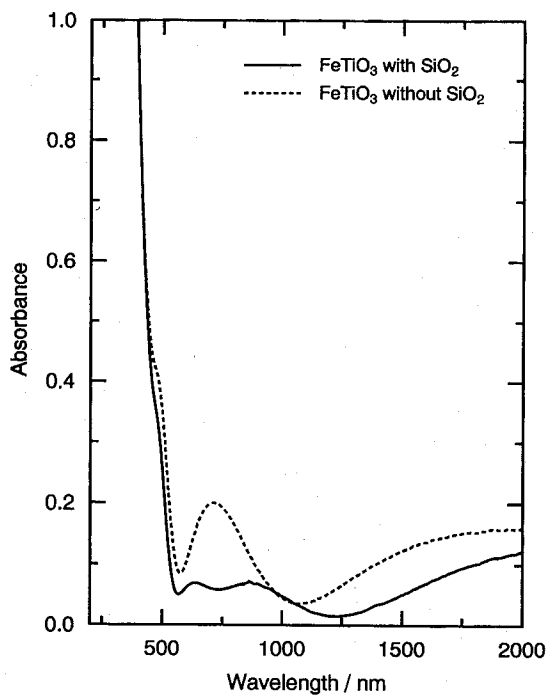


Fig. 4. Absorption spectra of FeTiO_3 thin films with and without additional SiO_2 coating.

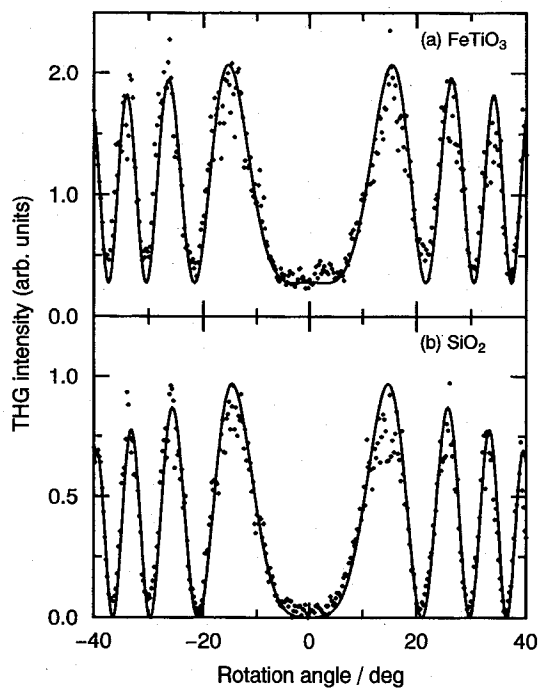


Fig. 5. THG intensities as a function of rotation angle for (a) FeTiO_3 film and (b) SiO_2 glass. Solid line is the best fitted curve for the plotted data.

SiO₂ glass in Figure 5. The THG intensity pattern of FeTiO₃ film clearly shows the interference between the THG lights from FeTiO₃ film and SiO₂ glass substrate as previously reported⁶⁾. The THG intensity was obtained by the least squares method as solid line in Fig. 5.

In the present study, $\chi^{(3)}$ value was determined by the equation⁹⁾

$$\chi_{\text{film}}^{(3)} = \frac{2}{\pi} \chi_{\text{SiO}_2}^{(3)} \frac{l_{\text{c, SiO}_2}}{l} \sqrt{\frac{I_{3\omega, \text{film}}}{I_{3\omega, \text{SiO}_2}}} \sqrt{\frac{n_{\omega, \text{film}}^3 n_{3\omega, \text{film}} T_{\omega, \text{SiO}_2}^3 T_{3\omega, \text{SiO}_2}}{n_{\omega, \text{SiO}_2}^3 n_{3\omega, \text{SiO}_2} T_{\omega, \text{film}}^3 T_{3\omega, \text{film}}}} \quad (\text{esu}), \quad (2)$$

where I denotes the THG peak intensity. The film thickness is used for l , because the film thickness is less than the coherence length. The values of $\chi_{\text{SiO}_2}^{(3)} = 2.8 \times 10^{-14}$ esu and $l_{\text{c, SiO}_2} = 18.1 \mu\text{m}$ were used for SiO₂ glass as both standard sample and substrate.¹⁰⁾

The intensity of THG signals generated from FeTiO₃ film was determined by the equation⁶⁾

$$I_{\text{film}} = \frac{I_{\text{max}} + I_{\text{min}}}{2} - \frac{I_{\text{substrate}}}{2} = \frac{I_{\text{max}} + I_{\text{min}}}{2} - \frac{I_{\text{SiO}_2}}{2}, \quad (3)$$

where I_{max} and I_{min} are the upper and lower envelopes of the superimposed THG intensity pattern. The contribution of THG light from the additional SiO₂ film on the FeTiO₃ film was neglected, because $\chi_{\text{SiO}_2}^{(3)}$ is low and the thickness of SiO₂ film (less than about $0.2 \mu\text{m}$) is much smaller than the coherence length. The $\chi^{(3)}$ value of FeTiO₃ film was determined to be 3.3×10^{-12} esu.

4. DISCUSSION

4.1 Relationship between $\chi^{(3)}$ and refractive index, n

It is possible to estimate $\chi^{(3)}$ of a material from refractive index, n , according to Miller's rule^{2,3)}

$$\chi^{(3)} = [\chi^{(1)}]^4 \times 10^{-10} \quad (\text{esu}), \quad (4\text{-a})$$

and

$$\chi^{(1)} = \frac{n^2 - 1}{4\pi}. \quad (4\text{-b})$$

The $\chi^{(3)}$ value calculated for FeTiO₃ film from Miller's rule was 7.6×10^{-13} esu, which is lower by a factor of about four than the measured $\chi^{(3)}$ value of 3.3×10^{-12} esu.

Figure 6 shows a relationship between $\chi^{(3)}$ and refractive index, n_{ω} , at 1,900 nm for FeTiO₃ thin film and other nonlinear optical materials reported so far.^{1,4,9-16)} It is seen that inorganic materials with high refractive index inherently exhibit high optical nonlinearity.

The $\chi^{(3)}$ values of organic polymers such as polydiacetylene (PDA)¹⁴⁾ and poly(2,5-dimethoxy *p*-phenylene vinylene) (MO-PPV)¹⁵⁾ deviate from the relation to a considerable extent, due to the enhancement by the so-called three-photon resonance or near three-photon resonance¹⁷⁾. Since the measured $\chi^{(3)}$ includes the significant contribution of the imaginary part, there are no simple relations between $\chi^{(3)}$ and refractive index for these organic materials, that is, Miller's rule does not hold.

4.2 Relationship between $\chi^{(3)}$ and optical band gap, E_g

One can expect that an enhancement in $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ occurs when in a material a frequency of interacting light approaches either one of one-, two- or three-photon resonance frequencies according to the relation¹⁷⁾

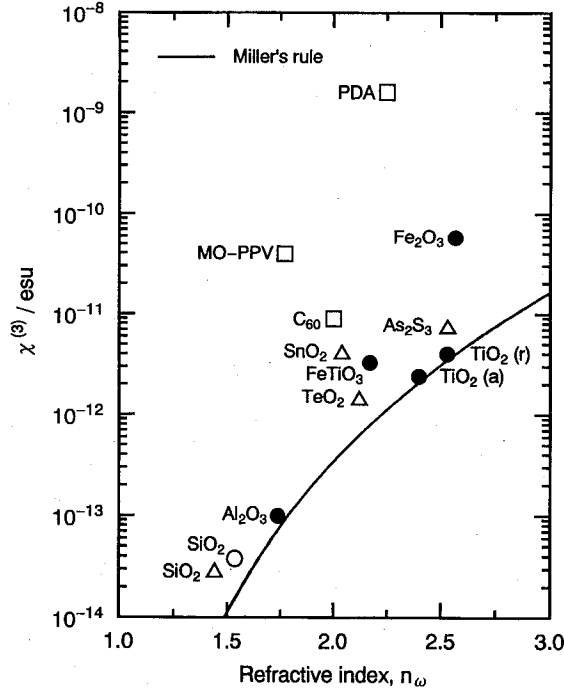


Fig. 6. Relationship between $\chi^{(3)}$ and refractive index, n_ω , at 1,900 nm for FeTiO₃ thin film and other nonlinear optical materials.^{1,4,9-16)} Circle, triangle and square denote inorganic crystal, inorganic amorphous material and organic material, respectively. Closed circles are the data measured by the present authors. The letters of r and a in parentheses denote rutile and anatase, respectively. PDA: polydiacetylene, MO-PPV: poly(2,5-dimethoxy *p*-phenylene vinylene).

$$\chi^{(3)}(-3\omega; \omega, \omega, \omega) \propto \frac{N}{\hbar} \sum_{g n m n'} \rho(g) F(\omega) \Omega_{gn} \Omega_{nm} \Omega_{mn'} \Omega_{n'g} \text{ (esu)}, \quad (5-a)$$

and

$$F(\omega) = \frac{1}{(E_{ng} - 3\omega)(E_{mg} - 2\omega)(E_{n'g} - \omega)} + \frac{1}{(E_{ng} + \omega)(E_{mg} - 2\omega)(E_{n'g} - \omega)} \\ + \frac{1}{(E_{ng} + \omega)(E_{mg} + 2\omega)(E_{n'g} - \omega)} + \frac{1}{(E_{ng} + \omega)(E_{mg} + 2\omega)(E_{n'g} + 3\omega)}, \quad (5-b)$$

where $\rho(g)$, E_{ij} and Ω_{ij} are the density matrix element of fundamental state, the energy difference between states i and j in \hbar ($=h/2\pi$, h : Planck's constant) unit and the transition matrix elements between states i and j , respectively. For materials having optical band gap, E_g , higher than three-photon energy, 3ω , the three-photon resonance makes the greatest contribution to the enhancement of $\chi^{(3)}$. Then, to a good approximation, the most significant term due to the three-photon resonance in Eq. (5) may be expressed as follows:

$$\chi^{(3)} = \frac{A}{(E_g - 1.96)(E_g - 1.31)(E_g - 0.65)} \text{ (esu)} \quad (E_g > 1.96), \quad (6)$$

where A is the phenomenological constant.

Figure 7 gives a relationship between $\chi^{(3)}$ and optical band gap, E_g , for FeTiO₃ thin film and

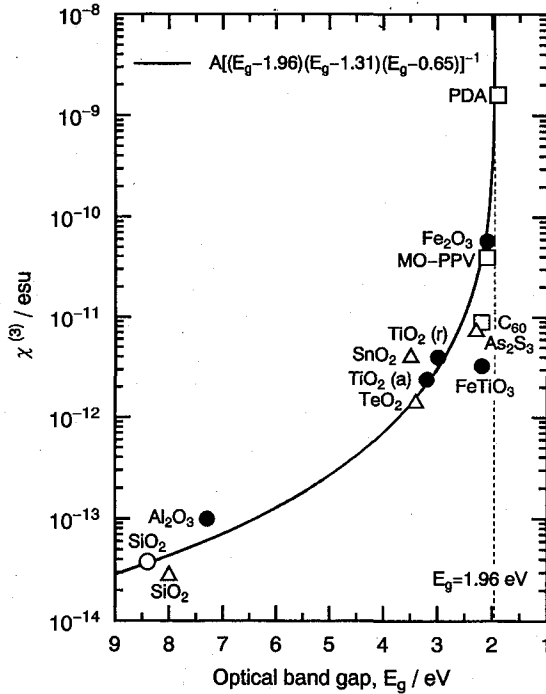


Fig. 7. Relationship between $\chi^{(3)}$ and optical band gap, E_g , for FeTiO₃ thin film and other nonlinear optical materials. References and notations are the same as in Fig. 6.

other nonlinear optical materials shown in Fig. 6. In Fig. 7, for organic materials the absorption edge of exciton absorption is used instead of E_g . In this figure, the $\chi^{(3)}$ values of these materials show a clear tendency to increase asymptotically as the E_g approaches 1.96 eV corresponding to the photon energy of THG signal. This change obeys Eq. (6) when the parameter, A , takes a value of 1.4×10^{-11} . The $\chi^{(3)}$ value calculated for FeTiO₃ film from Eq. (6) was 4.2×10^{-11} esu, which is higher by a factor of about ten than the measured $\chi^{(3)}$ value of 3.3×10^{-12} esu.

The above discussion indicates that the large $\chi^{(3)}$ value of 3.3×10^{-12} esu for FeTiO₃ film, which is comparable to those for TiO₂ polymorphs (rutile and anatase), is explained by the balanced contributions of two opposite effects, the lower refractive index (negative contribution) and the narrower optical band gap (positive contribution) compared with TiO₂ polymorphs. On the other hand, the $\chi^{(3)}$ value of FeTiO₃ film is one order of magnitude lower than that of α -Fe₂O₃ because of the lower refractive index and the wider optical band gap compared with α -Fe₂O₃.

4.3 Calculation of $\chi^{(3)}$ based on Lines' model

Lines introduced a bond-orbital theory dealing with the contribution of empty d orbital in addition to sp orbitals to linear and nonlinear optical properties, giving the following equation to estimate $\chi^{(3)}$ [18,19]:

$$\chi^{(3)} = \frac{25 \times 10^{-13} d^2 (n_\omega^2 - 1) f_L^3 E_S^6}{3\pi [E_S^2 - E^2]^4} \text{ (esu)} \quad (7)$$

where d denotes the bond length between cation and anion, $f_L = (n_\omega^2 + 2)/3$ the Lorentz local-field

correction factor, E_S the Sellmeier gap which is in practice equal to the average oscillator energy, E_0 , in Eq. (1). From Eq. (7), one can obtain $\chi^{(3)}$ value of 2.4×10^{-12} esu for FeTiO_3 film, which is in reasonable accordance with the measured value of 3.3×10^{-12} esu compared with those calculated by the above two empirical laws. This is possibly because two important optical properties (refractive index and Sellmeier gap) are included in Eq. (7).

Weak absorption bands around 1,100 nm (1.13 eV) and 800 nm (1.55 eV) due to the presence of Fe^{2+} and Fe^{3+} ions, respectively, do not always cause two-photon resonance at 1.31 eV, because the process requires parity opposite to one and three-photon related ones. Also, Kajzar et al.¹⁷⁾ reported that as for PDA films the effect of two-photon resonance on the third-order nonlinear optical susceptibility is smaller than that of three-photon resonance.

4.4 Effect of valence of Fe ion on third-order nonlinear optical properties

In order to make the effect of valence of Fe ions on the third-order nonlinear optical properties clear, microscopic second-hyperpolarizability, γ , is taken into account, because macroscopic $\chi^{(3)}$ depends on both γ_i and the number density, N_i of the i th constituents as follows^{20,21)}:

$$\chi^{(3)} = \frac{f_L^4}{24} \sum_i N_i \gamma_i \text{ (esu)}, \quad (8)$$

For a metal oxide, M_xO_y , γ per $\text{M}_{x/y}\text{O}$ formula unit, $\gamma(\text{M}_{x/y}\text{O})$, can be derived as follows:

$$\gamma(\text{M}_{x/y}\text{O}) = \frac{1944 \chi^{(3)} M_w}{N_A (n_w^2 + 2)^4 y D} \text{ (esu cm}^3\text{)} \quad (9)$$

where M_w , D and N_A are the molecular weight and density of M_xO_y and Avogadro's number, respectively.

Table 1. Microscopic and macroscopic nonlinear optical properties of FeTiO_3 thin film and other nonlinear optical materials.

	$\gamma(\text{M}_{x/y}\text{O})/\text{esu cm}^3$	$\chi^{(3)}/\text{esu}$	N_i/cm^{-3}	n_w	$D/\text{g cm}^{-3}$	$M_w/\text{g mol}^{-1}$
FeTiO_3	4.8×10^{-35}	3.3×10^{-12}	6.5×10^{22}	2.17	5.50	151.73
FeO^*	9.8×10^{-35}	—	—	—	—	71.85
$\alpha\text{-Fe}_2\text{O}_3^{(1)}$	3.5×10^{-34}	5.8×10^{-11}	5.9×10^{22}	2.57	5.26	159.70
TiO_2 (rutile) ⁽⁴⁾	2.5×10^{-35}	4.0×10^{-12}	6.4×10^{22}	2.53	4.23	79.88
TiO_2 (anatase) ⁽⁴⁾	2.2×10^{-35}	2.4×10^{-12}	5.9×10^{22}	2.40	3.89	79.88
SiO_2 glass ⁽¹⁰⁾	4.5×10^{-36}	2.8×10^{-14}	4.4×10^{22}	1.44	2.21	60.09

*: $\gamma(\text{FeO}) = 3\gamma(\text{Fe}_{1/3}\text{Ti}_{1/3}\text{O}) - 2\gamma(\text{Ti}_{1/2}\text{O})$.

The $\gamma(\text{Fe}^{2+}\text{O})$, $\gamma(\text{Fe}_{2/3}^{3+}\text{O})$ and $\gamma(\text{Ti}_{1/2}^{4+}\text{O})$ values were calculated using $\chi^{(3)}$ value of FeTiO_3 film, $\alpha\text{-Fe}_2\text{O}_3^{(1)}$ and $\text{TiO}_2^{(4)}$ to be 9.8×10^{-35} , 3.5×10^{-34} and $2.2\text{--}2.5 \times 10^{-35}$ esu cm³, respectively, as shown in Table 1. The $\gamma(\text{Fe}^{2+}\text{O})$ was one fourth to one third of $\gamma(\text{Fe}_{2/3}^{3+}\text{O})$. This may be ascribed to the smaller p - d overlapping resulting from the longer bond length of Fe-O. This long distance is due to the larger ionic radius of Fe^{2+} ion compared with Fe^{3+} ion. In fact, the bond lengths of Fe-O and Ti-O in FeTiO_3 are 2.09 and 2.03 Å,⁽²²⁾ respectively, whereas those in $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 are 2.03⁽²²⁾ and 1.95–1.96 Å,⁽²³⁾ respectively.

Since the Ti-O bond length in FeTiO_3 was assumed to be the same as that in TiO_2 on calculation of $\gamma(\text{Fe}^{2+}\text{O})$ value, the true $\gamma(\text{Ti}_{1/2}^{4+}\text{O})$ value for FeTiO_3 should be lower than that in

TiO₂ and then the $\gamma(\text{Fe}^{2+}\text{O})$ value should be larger than 9.8×10^{-35} esu cm³. Therefore, it can be said that the $\chi^{(3)}$ value of FeTiO₃ may be governed by the $\gamma(\text{Fe}^{2+}\text{O})$ rather than $\gamma(\text{Ti}_{1/2}^{4+}\text{O})$.

5. SUMMARY

The third-order nonlinear optical properties of the sol-gel derived FeTiO₃ thin films have been investigated by the THG method and the effect of the valence of Fe ions on the third-order nonlinear optical susceptibility has been examined. The following results were obtained.

(1) The $\chi^{(3)}$ value of FeTiO₃ thin film was 3.3×10^{-12} esu, which is comparable to those for TiO₂ polymorphs (rutile and anatase) but one order of magnitude lower than that of $\alpha\text{-Fe}_2\text{O}_3$. This was semiquantitatively interpreted in terms of the refractive index and optical band gap.

(2) The $\gamma(\text{Fe}^{2+}\text{O})$, which is one fourth to one third of $\gamma(\text{Fe}_{2/3}^{3+}\text{O})$, may be ascribed to the smaller p - d overlapping resulting from the longer bond length of Fe-O due to the larger ionic radius of Fe²⁺ ion compared with Fe³⁺ ion.

(3) The $\gamma(\text{Fe}^{2+}\text{O})$ was about four times as large as $\gamma(\text{Ti}_{1/2}^{4+}\text{O})$, indicating that the $\chi^{(3)}$ value of FeTiO₃ is governed by the $\gamma(\text{Fe}^{2+}\text{O})$ rather than $\gamma(\text{Ti}_{1/2}^{4+}\text{O})$.

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